

2771-696

**REMARKS****Summary of November 7, 2006 Office Action**

Claims 1-8, 11-14, 16-23, 27-31, 37-41, 43, 45-78, 80-93 and 97-112 are pending in the application, with claims 9, 10, 15, 24-26, 32-36, 42,44, 79, and 94-96 having been previously canceled. In the Office Action dated November 7, 2006, the rejection of all pending claims has been maintained. Specifically,

- ❑ claims 1-8, 11-14, 16-23, 27-31, 37-41 43 and 45-64 stand rejected under 35 USC 112, first paragraph, as failing to comply with the written description requirement.
- ❑ claims 65-84 and 88-96 stand rejected under 35 USC 102(b) as anticipated by Jin et. al. (US 6,479,100);
- ❑ claims 1-8, 11-14, 16-23, 27-31, 37-41 43 and 45-64 stand rejected under USC 103(a) as being unpatentable over Wade et. al. (US 6,440,495) in view of Shimamoto et. al. (US 6,743,739);
- ❑ claims 17-19, 43, 46 and 97-112 stand rejected under USC 103(a) as being unpatentable over Wade et. al. in view of Shimamoto et. al. in further view of Aaltonen et. al. (US 2003/0165615); and
- ❑ claims 85-87 stand rejected under USC 103(a) as being unpatentable over Jin et. al. in view of Aaltonen et. al. (US 2003/0165615).

By this response, claim 65 has been amended to include the requirement that the precursor/co-reactant gas mixture has an oxygen content of at least 30 mole percent. Support for this amendment is found in the specification (Paragraph 55) as well as claim 81. No new matter (35 USC 132) has been added and the claims, as now presented, are patentable over the art.

In addition, minor and self-evident grammatical errors in claims 108 and 109 have been corrected, as set out below:

108. (Currently amended) The method of ~~the~~ claim 107, wherein the second co-reactant gas comprises an oxygen:hydrogen gas mixture.

109. (Currently amended) The method of claim 108, wherein the ~~more~~ ratio of oxygen to hydrogen is from about 1:1 to about 1:3.

These corrections rectify obvious errors in grammar, and involves no addition of new matter (35 USC 132).

2771-696

**Non-Art Rejection of Claims and Traversal Thereof**

Claims 1-8, 11-14, 16-23, 27-31, 37-41 43 and 45-64 stand rejected under 35 USC 112, first paragraph, as failing to comply with the written description requirement.

The claims are said to contain subject matter which is not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

Specifically, it is stated that while the specification contains support for the provision of a ruthenium layer, it does not support the provision of a ruthenium metal layer under the newly added claimed processing conditions. It is contended that the newly added processing conditions to claims 1 and 3 are pertinent to a reaction under oxidizing conditions and, furthermore, that one of ordinary skill in the art would recognize such conditions as resulting in a ruthenium oxide layer and not a ruthenium metal layer.

Finally, it is stated that the recitation in claim 1 to a co-reactant gas is unsupported and that support only exists for oxygen and the combination of oxygen and hydrogen. Claims 2, 4-8, 11-14, 16-23, 27-31, 43 and 45-64 have been rejected as being dependent upon a rejected base claim.

Applicants respectfully traverse the rejection and request reconsideration. All of such prior amendments are fully supported by the specification and claims as filed.

The limitations recited in the specification and claims are applicable to the broad teaching of the specification. Contrary to the assertion of the Office, the process limitations introduced to claims 1 and 3 in the prior amendment are not limited to CVD under oxidizing conditions. Support for this position is found in the claims as filed. For example, the 250°C to 340°C temperature limitation incorporated in claim 1 was merely carried forward from original claim 3 as filed. Neither original claim 1 nor original claim 3 required oxidizing conditions.

In addition, although the Office Action asserts that there is only support for the co-reactant gas as oxygen or oxygen/hydrogen, original claims 6 and 11 support the broad concept of co-reactant gases, without any oxidation conditions limitation. While not previously presented in a dependent claim, the broader flow rate range recited in claim 3 is the range of flow rates that is set forth in Paragraph 56 of the specification. The narrower range of 15  $\mu\text{mol}/\text{min}$  to about 30  $\mu\text{mol}/\text{min}$  was presented in original claim 20, and does not require oxidizing conditions. Clearly, the specification and the claims as originally filed provide ample support for the claim amendments at issue.

2771-696

Finally, the Office Action contends that the conditions recited for the first deposition step in claim 1 will produce an oxide rather than a metal and, therefore, there is no support for the recitation to a metal. There is, however, no support for the Office's assertion that ruthenium oxide must be formed. Example 2, Process No. 3 in applicants' specification (see Table 2 on page 21 of the present specification) clearly shows that a suitable ruthenium metal nucleation layer is attained.

As further support, applicants enclose (in Appendix A hereof) a copy of an article entitled "Characterization of Ruthenium and Ruthenium Oxide Thin Films Deposited by Chemical Vapor Deposition for CMOS Gate Electrode Applications" by Filippou Papadatos et. al. (Mat. Res. Soc. Symp. Proc. Vol. 745, N3.3.1 (2003) which demonstrates that ruthenium metal layers may be deposited by CVD, even in the presence of high levels of oxygen.

In light of the foregoing discussion, and the specific support for the claims as amended, applicants respectfully request that the rejection of claims 1-8, 11-14, 16-23, 27-31, 37-41 43 and 45-64 under 35 USC 112, first paragraph, be withdrawn.

#### **Reference-Based Rejections of the Claims, and Traversal Thereof**

##### **Anticipation by Jin et. al.**

In the November 7, 2006 Office Action, the rejection of claims 65-84 and 88-96 under 35 USC 102(b) as anticipated by Jin et. al. (US 6,479,100) has been maintained.

The Office has reiterated its contention that Jin et. al. (column 4, lines 14-44) teach a method of forming a ruthenium film on a titanium nitride by depositing a ruthenium oxide seed layer followed by an annealing step that removes the oxygen content from the film layer and wherein the process is repeated to deposit subsequent layers. Further, the examples are said to anticipate all of the process conditions claimed by the applicants. It is stated that applicants' arguments of 29 September 2006 have been considered but are not persuasive, noting that applicants' arguments drawn to different processing conditions between layer depositions are not supported by the language in the claims.

Applicants respectfully traverse the rejection and request reconsideration.

As set forth in the prior response, it is well established, as a matter of law, that a claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a

2771-696

single prior art reference. *Verdegaal Bros. v. Union Oil Co. of California*, 2 U.S.P.Q.2d 1051, 1053 (Fed. Cir. 1987). Anticipation is not present here.

Contrary to the assertion of the Office, the cited text of Jin et. al., Col. 4, lines 14-44, makes **no mention whatsoever of repeating the process steps to form a ruthenium thin film**. The inference that repetitive steps are employed to build a 100 Angstrom seed layer is unfounded. The cited text only refers to the formation of a ruthenium oxide seed layer and employs just a single deposition step. Furthermore, nowhere is there any suggestion or inference that "Jin et. al. discloses repeating the ruthenium deposition process to create a layer with a final thickness of 100 A or less" as suggested by the Office (Paragraph 1 of the Office Action). Rather, as noted in Example 5 (Col. 9, lines 8-9), Jin et. al. teach that "Seed thickness is controlled by deposition times."

More importantly, Jin et. al. teach a two process method of forming ruthenium films on a substrate, the first being the formation of the CVD ruthenium oxide seed layer and the second being the deposition of the ruthenium film itself on the seed layer. Jin et. al. teach that each type of film to be deposited determines the oxygen:ruthenium ratio to be used, with a ratio of at least 10:1 needed for depositing the seed layer and a ratio of less than about 10:1 for the ruthenium thin film. Exemplary oxygen flow rates are given as 2500sccm per 180 mg/min precursor for the seed layer and 300 sccm per 180 mg/min for the ruthenium thin film (Col. 6, lines 48-64).

Applicants' prior arguments distinguishing over the art on the basis of different processing conditions between layer depositions refer to the Jin et. al. process, which clearly uses two different processes; applicants, by contrast, repeat their original process steps (see claim 65, reciting, inter alia, "**sequentially repeating steps (a) and (b) until the ruthenium thin film of desired thickness is deposited onto the substrate**").

Inasmuch as Jin et. al. do not specifically teach or suggest a repetitive process or the process conditions of applicants' method, the anticipation rejection of Claims 65-84 and 88-96 fails and amended independent claim 65, and all claims dependent thereon, as now presented, are patentable over Jin et. al. Applicants respectfully request that the rejection be withdrawn and that claims 65-78 and 80-93 be allowed.

2771-696

**Obviousness over Wade et. al. in view of Shimamoto et. al.**

In the November 7, 2006 Office Action, claims 1-8, 11-14, 16-23, 27-31, 37-41 43 and 45-64 stand rejected under USC 103(a) as being unpatentable over Wade et. al. in view of Shimamoto et. al. (US 6,743,739).

Wade is said to teach a method of forming a ruthenium film on a titanium nitride surface by CVD wherein a ruthenium oxide layer is deposited by CVD prior to the bulk layer. It is stated that the examples and tables of Wade anticipate all of applicants' processing conditions but fail to teach using a ruthenium metal layer as a seed layer.

Shimamoto et. al. is said to teach the use of a ruthenium metal seed layer in order to control the oxygen content in the resulting film.

According to the Office, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify Wade et. al. to include a ruthenium metal seed layer as taught by Shimamoto et. al. to control the oxygen content of the resulting film.

As set forth in applicants' prior response, Wade et. al. teach a method of forming ruthenium films by CVD in a kinetically limited temperature regime. Though an objective of Wade et. al. is to avoid the need for a seed layer, especially a ruthenium seed layer, (see Table 1, Column 7, line 18), Wade et. al. repeatedly teach of the importance and benefits of the use of a PVD (physical vapor deposition) seed layer.

For example, at column 10, lines 42-45, Wade et. al. state **"The lower activation energies and higher deposition rates on PVD Ru highlight the importance of using a PVD Ru seed layer as a substrate for CVD Ru growth."** At column 14, lines 44-45, Wade et. al. state "[U]sing the same process conditions, **the surface morphology was improved by using a thin PVD Ru seed layer....**". At column 16, lines 12-13, Wade et. al. state **"By depositing CVD Ru onto a PVD Ru seed layer, the film roughness and step coverage can be greatly reduced."** It is acknowledged that Wade et. al. mention CVD of a ruthenium oxide as a possible seed layer; however, this is just one of a host of possible seed layer materials and methods identified. Furthermore, the only seed layer specifically taught by Wade et. al. is PVD of ruthenium metal, a process which is extolled by Wade et al. for its many attributes. Wade et. al. makes clear that a PVD ruthenium seed layer is paramount. Perhaps the most telling of indicators as to the state of the art relating to ruthenium seed layer formation is the statement in Table 1 (column 7,

2771-696

line 18) of Wade et. al. that the "Current Best Known Method" for Ru CVD film formation "requires PVD seed layer."

Reliance on Shimamoto et. al. does not support a case of *prima facie* obviousness. Contrary to the assertion of the Office, Shimamoto et. al. nowhere mentions or in any way suggests the use of CVD for the generation of a seed layer, let alone of a ruthenium metal seed layer as required by the present claims. Indeed, the text cited by the Office (Col. 4, lines 3-14) merely references the importance of a seed layer and, like Wade et. al., identifies a number of different seed layer materials including ruthenium. Only the second citation, Col. 5, line 66 to Col. 6, line 17, references the seed layer formation method, sputtering - a PVD process. This method is reinforced throughout the detailed description, e.g., Col. 7, lines 35-38; Col. 8, lines 64-66, and in the examples, all of which employ a sputtered ruthenium seed layer. Shimamoto et. al.'s use of a PVD ruthenium seed layer is consistent with Wade et. al.'s teaching of PVD seed layers as being the "current best known technology."

Thus, the combined teachings of Wade et. al. and Shimamoto et. al. yield no suggestion or motivation for one to employ a CVD ruthenium metal nucleation layer. Indeed, the disclosures of such references would logically lead one to employ a PVD ruthenium seed layer, as the "current best-known technology." As discussed in applicants' prior response, applicants are able to provide a ruthenium metal nucleation layer on a substrate by use of conditions including, as claimed, a ruthenium precursor/co-reactant gas mixture comprising at least 30 mole % oxygen content, deposition temperatures of from 250°C to 340°C, and a precursor flow rate that, under the deposition conditions, provides for a surface reaction-rate limited deposition. None of these conditions are in any way suggested, shown or specified in Wade et. al. or Shimamoto et. al., nor is there any suggestion, motivation or derivative basis in either of these references for the use of CVD for deposition of a ruthenium metal seed layer.

In light of the foregoing, it is clear that the Office has failed to establish *prima facie* obviousness.

Nowhere has the Office shown any motivation for the formation of a ruthenium-based seed or nucleation layer by CVD, nor, more specifically, of a ruthenium metal nucleation layer by CVD.

Further, there is no suggestion, inference or expectation that the combined use of a CVD ruthenium metal nucleation layer with a CVD ruthenium metal film layer will provide ruthenium films of superior adherence and resistivity, as achieved by applicants' claimed invention (see examples at pages 19-24 of applicants' specification).

2771-696

Based on the above, claims 1-8, 11-14, 16-23, 27-31, 37-41 43 and 45-64 are patentably distinguished over the art. It therefore is requested that the rejection of such claims be withdrawn.

**Obviousness over Wade et. al. in view of Shimamoto et. al. in further view of Aaltonen et. al.**

In the November 7, 2006 Office Action, the rejection was maintained of claims 17-19, 43, 46 and 97-112 under 35 USC 103(a) as being unpatentable over Wade et. al. in view of Shimamoto et. al. (US 6,743,739) in further view of Aaltonen et. al. (US 2003/0165615). The Office has contended that Wade et. al. and Shimamoto et. al. teach all of the limitations of applicants' invention and claims except for specifically teaching the use of Ru(thd)<sub>3</sub> as the ruthenium precursor. Aaltonen et. al. are said to teach the art recognized suitability of using Ru(thd)<sub>3</sub> as the ruthenium precursor.

The Office contends that it would have been obvious to one of ordinary skill in the art to use Ru(thd)<sub>3</sub> as the ruthenium precursor in Wade et. al. and, in doing so, have a reasonable expectation of success.

Applicants respectfully traverse such rejection and request reconsideration.

As set forth above, neither Wade et. al. nor Shimamoto et. al., individually or combined, teach or make obvious applicants' method of forming a ruthenium metal film on a substrate, wherein the ruthenium metal film comprises a ruthenium metal seed layer and a upper ruthenium metal film layer, wherein the layers are formed by CVD under two different sets of conditions, the first being conditions that favor formation of a ruthenium metal film, even in the presence of oxygen, that is suitable for and acts as a seed or nucleation layer, and the second being conditions that form a ruthenium metal film of low resistivity.

Neither Wade et. al. nor Shimamoto et. al. teaches or suggests the formation of a seed layer by CVD – indeed, both exemplify and provide specific teaching only for ruthenium PVD seed layers, and both emphasize the importance of such ruthenium PVD seed layers.

While the Office further attributes the formation of ruthenium oxide seed layers to Wade et. al., nowhere in such reference is there any suggestion, teaching or motivation whatsoever of the preparation of a **ruthenium metal nucleation layer by CVD**.

Aaltonen et. al. does not overcome this deficiency, since Aaltonen et. al. is specifically directed to the atomic layer deposition (ALD) of ruthenium metal films. Aaltonen et. al. is cited as motivation for the substitution/selection of Ru(thd)<sub>3</sub> as the ruthenium precursor in the method of Wade et. al. and

2771-696

Shimamoto et. al. Even if there were a reason or motivation to make the substitution (although no basis for such substitution is apparent on the basis of the referenced teachings themselves), one would still not arrive at applicants' claimed invention, since the process hypothesized by the Office fails to teach, suggest or motivate a CVD ruthenium metal nucleation layer in combination with a CVD ruthenium metal bulk layer as claimed.

In light of the foregoing, it is apparent that the Office has failed to establish a case of *prima facie* obviousness. Such obviousness determination requires a finding of each element of the claimed invention in a plurality of references, yet no such finding is presented here.

The presently claimed invention is neither embraced by nor an obvious variant of the teachings of either the primary or the secondary references or of their combined teachings. Merely substituting one ruthenium precursor for another does not in any way yield or extrapolate to the claimed method. The obviousness rejection of claims 17-19, 43, 46 and 97-112 therefore should be withdrawn.

**Obviousness over Jin et. al. in view of Aaltonen et. al.**

In the November 7, 2006 Office Action, the rejection of claims 85-87 under 35 USC 103(a) as being unpatentable over Jin et. al. (US 6,479,100) in view of Aaltonen et. al. (US 2003/0165615) has been maintained. It is again alleged that Jin et. al. teaches all of the limitations of applicants' claimed invention except for specifically teaching the use of Ru(thd)<sub>3</sub> as the ruthenium precursor. Aaltonen et. al. is said to teach the art recognized suitability of using Ru(thd)<sub>3</sub> as the ruthenium precursor. The Office contends that it would have been obvious to one of ordinary skill in the art to use Ru(thd)<sub>3</sub> as the ruthenium precursor in Jin et. al. and, in doing so, have a reasonable expectation of success.

Applicants respectfully traverse such rejection and request reconsideration.

As discussed above, Jin et. al. does not teach, nor does it make obvious, applicants' method of forming a ruthenium metal film on a substrate by repeatedly performing a two step process of depositing a ruthenium nucleation layer in an oxygen rich, at least 30 mole % oxygen, environment by CVD, followed by deoxygenation of the deposited ruthenium nucleation layer to produce a ruthenium film.

Unlike applicants' method, in which these same process steps are repeatedly carried out to build the desired ruthenium layer, Jin et. al. forms a ruthenium oxide seed layer by a process involving a high oxygen content followed by annealing, and then builds a ruthenium thin film on the annealed seed layer



2771-696

by ruthenium deposition under oxygen-free or oxygen-depleted conditions, with no disclosed annealing. The Jin et al. process thus involves fundamentally different conditions from those claimed by applicants.

Further, the method claimed by applicants is contrary to the express teachings of Jin et. al.

Specifically, Jin et. al. teaches that the seed layer thickness is critical to ensure that the subsequently deposited ruthenium film does not peel off (Col. 9, lines 7-19). Thus, one would not be motivated to simply repeat Jin et al.'s seed deposition and annealing process over and over to build a ruthenium layer on a substrate, since the logical result of such processing would be that subsequent layers would peel apart from one another.

As noted in applicants' prior response, Aaltonen, et. al. does not overcome these deficiencies, since Aaltonen, et. al. is directed to ALD of ruthenium metal films. Thus, even if there were a reason or motivation for the substitution/selection of Ru(thd)<sub>3</sub> as the ruthenium precursor in the method of Jin et. al. (although such is not in any way taught or suggested in the cited references), one still would not arrive at applicants' claimed invention.

In light of the foregoing discussion, the Office has failed to establish a case of *prima facie* obviousness.

A determination of *prima facie* obviousness requires a finding of each element of the claimed invention in a plurality of references, yet no such finding is presented here.

The presently claimed invention is neither embraced by nor an obvious variant of the teachings of the primary reference or its combination with Aaltonen, et al. Merely substituting one ruthenium precursor for another in the Jin et al. process provides no derivative basis for the applicants' claimed method.

Accordingly, the obviousness rejection of claims 85-87 should be withdrawn.

### CONCLUSION

Applicants have satisfied all requirements for patentability. The pending claims are free of the art and fully comply with the requirements of 35 U.S.C. §112, §102, and §103.

It therefore is requested that Examiner Stouffer reconsider the patentability of the pending claims in light of the amendment made to claim 65 and the distinguishing remarks presented herein, and withdraw the rejections made in the November 7, 2006 Office Action.

2771-696

A Notice of Allowance is merited and respectfully requested.

Should any issues remain, Examiner Stouffer is requested to contact the undersigned attorney at (919) 419-9350 to resolve same, so that this application can be passed to issue at an early date.

Respectfully submitted,



Steven J. Hultquist  
Reg. No. 28021  
Attorney for Applicants

**INTELLECTUAL PROPERTY/  
TECHNOLOGY LAW**  
Phone: (919) 419-9350  
Fax: (919) 419-9354  
Attorney File No.: 2771-605 (7486)

## APPENDIX A

## Characterization of Ruthenium and Ruthenium Oxide Thin Films deposited by Chemical Vapor Deposition for CMOS Gate Electrode Applications

Filippos Papadatos, Spyridon Skordas, Steve Consiglio, Alain E. Kaloyeros, and Eric Eisenbraun  
*University at Albany Institute for Materials and School of NanoSciences and NanoEngineering  
Albany, NY 12203, U.S.A.*

### ABSTRACT

This study describes work carried out to date involving evaluation of the chemical, structural, and electrical performance of ruthenium (Ru) and ruthenium oxide (RuO<sub>2</sub>) films grown on SiO<sub>2</sub> substrates employing metal organic chemical vapor deposition (MOCVD). Diethyl ruthenocene and oxygen were employed as reactant gases for this work, which was carried out using a 200-mm wafer cluster tool. The films were characterized using cross-sectional scanning electron microscopy (CS-SEM), four-point resistance probe, x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), x-ray diffraction (XRD), and energy dispersive spectrometry (EDS). Capacitance-voltage (C-V) measurements were also carried out to assess the work function of the deposited films. It was determined that both Ru and RuO<sub>2</sub> phases possess near-bulk resistivity and low contamination levels. Importantly, it was observed that the film stoichiometry could be modulated by controlled changes of the processing conditions, and that pure Ru and RuO<sub>2</sub> films can be deposited in an oxygen ambient. In order to assess thermal stability, the films were subsequently annealed in forming gas and oxygen ambients, and it was found that the film stability is dependent upon both the deposited phase and the annealing ambient. Results of PMOS gate electrode performance testing of CVD Ru films, has been carried out, and the results are similar to those previously reported for ruthenium-based films.

### INTRODUCTION

Ru and RuO<sub>2</sub> are attractive materials for CMOS gate electrode applications. These films exhibit low resistivity (7 and 46  $\mu\Omega\text{-cm}$  for Ru and RuO<sub>2</sub>, respectively) and demonstrate good thermal stability not only on SiO<sub>2</sub> but also on other high-k materials such as ZrO<sub>2</sub> [1,2,3,4]. Sputter-deposited Ru and RuO<sub>2</sub> films have been evaluated for gate electrode applications; however, the damage intrinsic in such processes is potentially problematic for applications employing ultra-thin gate dielectrics due to possible interface damage [5]. Moreover, sputtered Ru-based films typically possess high levels of compressive stress, causing potential reliability concerns [6]. As such, a low-temperature metal organic chemical vapor deposition (MOCVD) approach is attractive for these applications. This work describes the evaluation of MOCVD Ru and RuO<sub>2</sub> films grown for gate electrode applications; including determination of stoichiometry, resistivity, and thermal stability. Electrical measurements to investigate the work function of Ru-based films are also described.

### EXPERIMENTAL DETAILS

The 200-mm cluster tool and the warm-wall MOCVD reactor utilized in this study have been described in previous work [7]. The precursor used in this work was diethyl ruthenocene

## N3.3.2

[Ru(C<sub>5</sub>H<sub>4</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>], which is a room-temperature liquid, and has relatively high vapor pressure at low temperatures (~ 10 Torr at 110°C). It is also thermally stable up to approximately 250°C, thus allowing a wide temperature range for vapor delivery. As such, it is attractive for chemical vapor deposition applications. In these experiments the temperature of the precursor reservoir was kept at 120°C, providing adequate precursor flow for the depositions. The delivery lines and the chamber walls were kept ~20°C above the reservoir temperature to minimize precursor recondensation. Precursor flow was metered using an MKS 1153A low vapor pressure source mass flow controller. Hydrogen and oxygen were both evaluated as co-reactants for the growth of Ru-based films using this precursor.

In order to characterize the MOCVD-deposited films, a variety of analytical techniques were employed. Thickness was measured by cross sectional scanning electron microscopy (CS-SEM) on a Hitachi S4000 field emission SEM operating at 10kV, while sheet resistance was measured with a Prometrix RS35c four-point probe mapper. Composition and stoichiometry were determined by x-ray photoelectron spectrometry (XPS) in conjunction with Rutherford backscattering spectrometry (RBS) and energy dispersive spectrometry (EDS). XPS was performed using a PHI 5500 system, employing Mg K $\alpha$  photons (1253.6 eV) at a power of 300 Watts. Depth profiling was achieved via the use of an Ar ion sputtering gun. RBS was carried out using the UAlbany Dynamitron, employing He<sup>2+</sup> ions at 2 MeV energy. EDS was performed using a Noran EDS system mounted on the Hitachi S4000 SEM. The crystal phase was examined by x-ray diffraction (XRD) using a Scintag XDS 2000, and capacitance-voltage (C-V) measurements were performed on metal-oxide-semiconductor (MOS) capacitor structures to determine the work function of the Ru films.

To assess thermal stability of the films in reducing and oxidizing ambients, CVD Ru and RuO<sub>2</sub> samples were annealed in high purity oxygen or forming gas (5% hydrogen in argon) for one hour at 650°C. The samples were then re-characterized to determine any thermally-induced electrical, chemical, or structural changes.

## DISCUSSION

### Role of Processing Conditions on Film Properties

Table I lists the range of processing conditions employed in testing the CVD Ru and RuO<sub>2</sub> processes, using thermally grown SiO<sub>2</sub> as the substrate material. It was found that no film could be deposited using hydrogen as a co-reactant in the process range investigated, indicating that neither a simple thermal decomposition nor a reduction mechanism are involved in the reactivity of this precursor. On the other hand, it was found that oxygen could be used to deposit both ruthenium and ruthenium oxide films, through simple changes to the processing conditions. In particular, it was found that wafer temperature had a significant impact on deposited phase. Specifically, oxygen incorporation in the film increases as a function of wafer temperature over the range from 340°C to 480°C. At the conditions explored herein, wafer temperatures below approximately 400°C yielded predominantly Ru phase films, and above 400 °C yielded predominantly RuO<sub>2</sub> phase films. This is evidenced by XPS and XRD measurements shown in Figures 1 and 2, respectively, for films deposited at 340°C (Ru phase) and 480°C (RuO<sub>2</sub> phase). The specific role of wafer temperature in the precursor decomposition mechanism is still under investigation; however, it is believed that at low temperatures, the oxygen serves to liberate the ethylcyclopentadienyl ligand from the precursor, while at higher temperatures the reactivity of

## N3.3.3

Table I. Process parameters investigated for the MOCVD growth of Ru and RuO<sub>2</sub>.

<b>Ru precursor</b>	<b>Ru(C<sub>2</sub>H<sub>5</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub></b>
<b>Deposition temperature</b>	<b>340 to 480°C</b>
<b>Reactive gas (O<sub>2</sub> or H<sub>2</sub>) flow rate</b>	<b>50 to 300 sccm</b>
<b>Deposition pressure</b>	<b>0.3 to 2 Torr</b>
<b>Precursor flow rate</b>	<b>1 to 2 sccm</b>

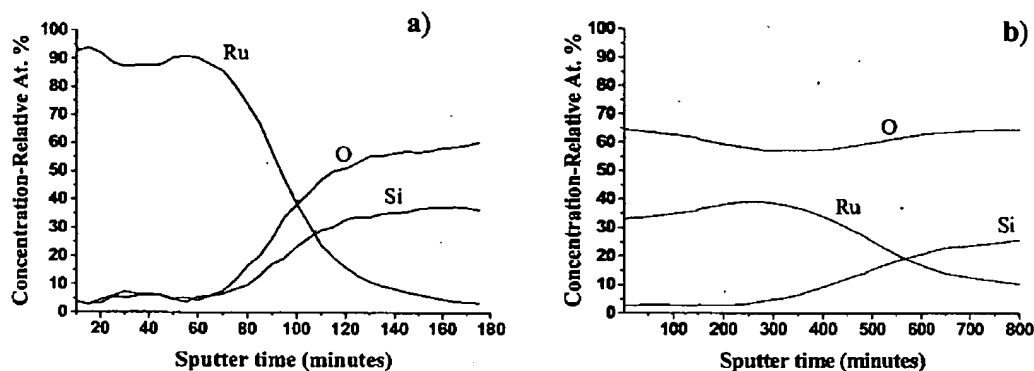


Figure 1. X-ray photoelectron spectroscopy (XPS) measurements of Ru-based films deposited at a) 340°C and b) 480°C on SiO<sub>2</sub>, displaying the role of wafer temperature on deposited phase. The XPS data has been smoothed.

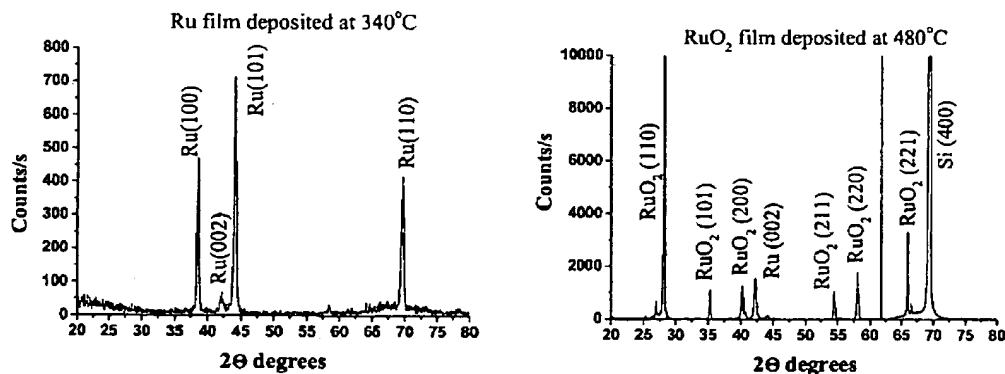
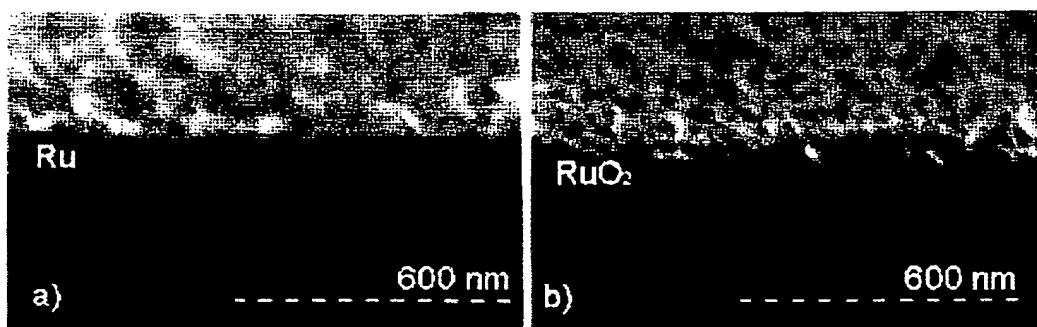


Figure 2. XRD spectra for Ru (left) and RuO<sub>2</sub> (right) films, confirming the effect of substrate temperature on deposited ruthenium phase.

## N3.3.4



**Figure 3.** Cross-section SEM images of a) 120 nm thick CVD Ru and b) 120 nm thick CVD RuO<sub>2</sub> films. The Ru exhibits a smooth microstructure with small grains, while the RuO<sub>2</sub> shows a more pronounced columnar structure.

oxygen is such that it directly reacts with the ruthenium metal. Additionally, the fact that no film deposition occurs in the absence of oxygen over a wide range of temperature values, clearly demonstrates oxygen's importance in the overall reaction. This was also supported by the observation that the film growth rate also increased with oxygen flow rate.

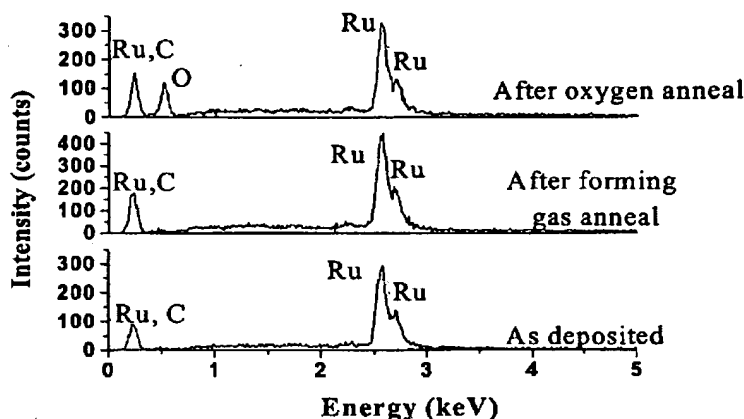
The lowest resistivities achieved for Ru and RuO<sub>2</sub>-phase material were  $\sim 10 \mu\Omega\text{-cm}$  and  $\sim 47 \mu\Omega\text{-cm}$ , respectively. These compare very favorably with the bulk values for both materials. It should be noted that due to coincidental peak overlaps between ruthenium and carbon, it is very difficult to accurately quantify the level of carbon incorporated into the films. However, XPS peak deconvolution and separate resonance RBS measurements indicated low levels (i.e. <5 atomic %) of carbon contamination. Furthermore, the near-bulk resistivity values of the films also suggest that these films possess low concentrations of contaminants and high densities. Figures 3, a and b are cross-section SEM images of 120-nm thick MOCVD-grown Ru and RuO<sub>2</sub> films. The MOCVD-grown Ru films exhibit a smooth, dense microstructure, while the RuO<sub>2</sub> films exhibit a more distinct columnar structure.

### Thermal Stability

To carry out an evaluation of the thermal stability of these films, representative MOCVD Ru and RuO<sub>2</sub> samples were divided into two pieces. One piece was annealed in a UHP forming gas ambient (5% hydrogen, 95% Argon) for 60 min at 650°C and 700 torr, while the other one was annealed under the same conditions in oxygen ambient. After anneal, the film properties were re-characterized and compared to the as-deposited samples.

In the reducing ambient (forming gas) anneal, the RuO<sub>2</sub> films were observed to delaminate. One proposed reason for this is stresses related to forming gas reduction of the RuO<sub>2</sub> film, which is known to occur in this temperature range [8]. By comparison, Ru films thus annealed did not exhibit delamination, and in fact exhibited resistivity reductions by as much as 38%. This reduction in the resistivity is under investigation, and is attributed either to the elimination of residual contaminants such as carbon and hydrogen, or reduced grain boundary scattering enabled by grain growth. In contrast, in the oxidizing ambients the RuO<sub>2</sub> films exhibited a reduction in resistivity by as much as 17%. The exact mechanism for this reduction is also under investigation, and may again be attributed to elimination of contaminants and/or grain growth.

N3.3.5



**Figure 4.** EDS spectra of a Ru film demonstrating the effect of forming gas and oxygen annealing on the composition of the films. The films are stable after 650°C FGA, and exhibit increased oxidation after oxygen anneal. Ru and C peak overlap is noted.

The Ru films annealed in oxygen exhibited an increase in the oxygen content, but the measured film resistivity did not increase. Figure 4 shows EDS spectra for an as deposited Ru film, as well as that sample after forming gas and oxygen anneals. The primary change observed is the increase in oxygen incorporation in films annealed in oxygen.

#### Work function measurements

To carry out the work function measurements, MOS capacitors structures were formed by depositing 1mm diameter CVD Ru dots through a contact mask on thermally grown SiO<sub>2</sub> with thickness values from 2.5 nm to 72.5 nm. The underlying substrates were p-type Si with doping levels of approximately  $3 \times 10^{15}$  atoms/cm<sup>3</sup>. The thickness of the SiO<sub>2</sub> was confirmed using single wavelength ellipsometry, with a resulting error of less than 10%. There was no treatment of the SiO<sub>2</sub> substrates prior the CVD Ru deposition. After the C-V measurements were performed, the flatband voltage shift was determined for each sample and plotted as a function of oxide thickness. From this, the workfunction deference between the metal and the semiconductor ( $\Phi_{ms}$ ) was determined [9]. Figure 5a shows a representative C-V curve measured at 100 kHz for a Ru dot on top of the 21.9 nm thick SiO<sub>2</sub> sample, and Figure 5b shows the resulting plot of the flatband voltage shift as a function of oxide thickness. This data yielded a metal-semiconductor workfunction difference ( $\Phi_{ms}$ ) of 0.46 V, corresponding to a Ru workfunction of 5.3 eV.

Additional data sets will be processed to confirm this value, and the same measurements will be carried out using RuO<sub>2</sub> electrodes, which are expected to yield similar values as Ru.

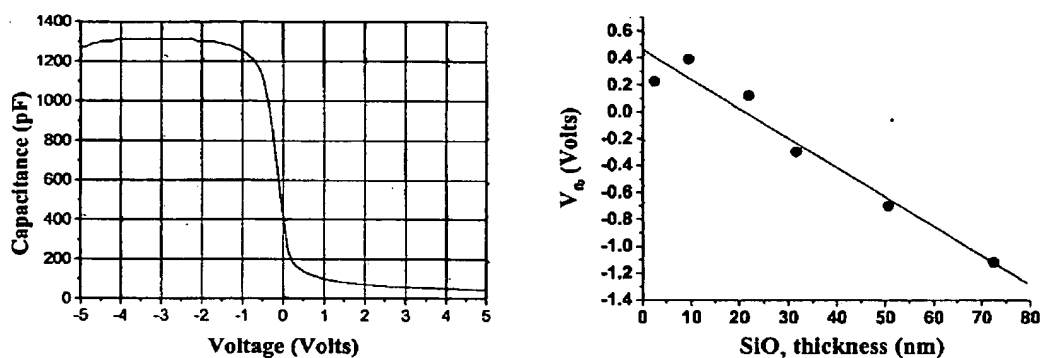
#### **CONCLUSIONS**

MOCVD-grown Ru and RuO<sub>2</sub> films have been characterized to determine their applicability for emerging CMOS gate electrode applications. It was found that the resulting films possess low



N3.3.6

contamination and near-bulk resistivity values, were smooth and dense, and that the deposited phase could be controlled by modulating the processing conditions. The thermal stability of the films depends upon the deposited phase and the subsequent annealing ambient, and are stable up to at least 650°C depending upon the ambient. Electrical measurements indicate that CVD Ru films possess workfunction values appropriate for PMOS applications.



**Figure 5.** a) C-V plot for Ru gate electrode deposited on 21.9nm thick  $\text{SiO}_2$ . b) Flat band voltage plotted versus  $\text{SiO}_2$  thickness, resulting in a calculated Ru workfunction of 5.3 eV.

#### ACKNOWLEDGEMENTS

This work was funded by SEMATECH and the Semiconductor Research Corporation (SRC) under the Front End Processing Research Center, which is gratefully acknowledged.

#### REFERENCES

- 1 H. Zhong, G. Heuss, and V. Misra *IEEE Electron Device Lett.* **21**,593 (2000).
- 2 H. Zhong, G. Heuss, and V. Misra, H. Luan, C. Lee, and D. Kwong, *Appl. Phys. Lett.* **78**, 1134 (2001).
- 3 T. Takagi, I. O. Ichizo K. and M. Okada, *Jpn. J. Appl. Phys.*, **34**, 4103 (1995).
- 4 A. J. Hartmann et al *Appl. Phys A*, **70**, 293 (2000).
- 5 G. D.Wilk, R. M. Wallace, J. M. Anthony, *J. Appl. Phys.*, **89**, 5243-5275 (2001).
- 6 L. Meng, M. P. Santos, *Appl. Surf. Sci.* **147**, 94 (1999).
- 7 F. Papadatos, S. Skordas, Z. Patel, S. Consiglio, and E. Eisenbraun, in *Silicon Materials Processing-Characterization and Reliability*, edited by J. Veteran, D.L. O'Meara, V. Misra, and P. Ho, (Mater. Res. Soc. Proc. **716**, San Francisco, CA, 2002) pp.79-84.
- 8 H. Madhavaram, H. Idriss, S. Wendt, Y. D. Kim, M. Knapp, H. Over, J. Assmann, E. L. Loffler and M. Muhle, *J. Catal.* **10**, 1006 (2001).
- 9 E.H Nicollian, and J.R Brews, *MOS Physics and Technology*, (John Wiley & Sons, New York, 1982), p.469.